THE PREPARATION AND DEHYDROGENATION OF SPIRANS

BY

LESTER ALLEN BROOKS

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INTRODUCTION

The cyclization of dienynes[1] and suitable tertiary alcohols[2,3] has been stated to lead to the formation of phenanthrene derivatives. This belief has been based upon the results of dehydrogenation studies.

The structure of these products has been the subject of controversy. Increasing interest is being shown in the possibility that these compounds may be spirans or mixtures of these and phenanthrene derivatives. There is some indication that compounds of the spiran type may be dehydrogenated to aromatic hydrocarbons.[4] This would then indicate that the products obtained under dehydrogenation conditions need not necessarily arise from the hydroaromatic parent compound but also might result from the rearrangement and dehydrogenation of a spiran. These new facts weaken the evidence for the structures assigned to certain hydroaromatic ring systems prepared by ring closure methods.

In order to clear up some of these structural problems, the synthesis of several spirans has been attempted in order to study the products obtained under various dehydrogenation conditions.

EXPERIMENTAL AND DISCUSSION

Spirodecane was prepared in a manner similar to the preparation of 1,1-dimethyl cyclohexene-3 as described by Linstead and Hibbit.[5] The reaction between cyclopentanone and the Grignard reagent of 1-bromopentene-4 produced 1-(pentene-4) cyclopentanol. Dehydration by distillation from a crystal of iodine produced the diene cyclopentylidene-1-pentene-4. Cyclization of the diene to impure spirodecene-7 was effected using 82 per cent sulphuric acid. The spirodecene-7 was contaminated with an ether presumably 2,2-spirocyclopentane-6-methyl tetrahydropyran.[6] Pure spirodecane was obtained by reduction of the spirodecene-7 over Raney nickel at 175° and 1900 lbs., followed by washing with a concentrated sulphuric acid-oleum mixture. This compound was identical with that described by Zelinsky and Schuikin[7] with the exception that it did not react with bromine.

Spirodecane could not be dehydrogenated over selenium[8] at 355° but dehydrogenated readily over platinum and palladium at 325° to give a 33 per cent and 35 per cent yield of naphthalene, respectively.

3-Methyl spirodecane was prepared in a similar manner. Pulegone → β-methyl adipic acid → 3-methyl cyclopentanone → 3-methyl-1-(pentene-4)-cyclopentanol → 3-methylcyclopentylidene-1-pentene-4 → 3-methyl spirodecene-7 plus an ether → 3-methyl spirodecane.

3-Methyl spirodecane could not be dehydrogenated over selenium at 330° but dehydrogenated readily over palladium at 325° to give a 31 per cent yield of 2-methyl naphthalene. No 1-methyl naphthalene or naphthalene could be detected.

SUMMARY

Evidence has been presented that the use of dehydrogenation experiments employing platinum and palladium to prove the structure of hydroaromatic compounds prepared by cyclization methods where spiran formation is also possible, may now be considered to be of uncertain value.

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VITA

The writer was born in Allston, Massachusetts, on May 20, 1914. He attended the Washington Allston grammar school and was graduated from Boston English High School in 1931. He received the degree of Bachelor of Science in Chemical Engineering from the Massachusetts Institute of Technology in 1935. From 1935 to 1937 he was employed by the Hooker Electrochemical Company, Niagara Falls, New York. In 1937 he entered the Graduate School of the University of Illinois and held an appointment in the U. S. Regional Soybean Laboratory from 1938 to 1939. From 1939 to the present date he has been an assistant in chemistry at the University of Illinois, while studying for the degree of Doctor of Philosophy.

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